
Further Test of the Isolated Pentagon Rule: Thermodynamic and Kinetic Stabilities of C₈₄ Fullerene Isomers

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ABSTRACT

Thermodynamic and kinetic stabilities of 73 C₈₄ fullerene isomers were estimated from the MM3 heats of formation and the recently defined bond resonance energies (BREs), respectively. The BRE represents the contribution of a given π bond in a molecule to the topological resonance energy (TRE). All π bonds shared by two pentagons turned out to be highly reactive without exceptions. C₈₄ fullerene isomers with such π bonds must be incapable of survival during harsh synthetic processes. Thus, the isolated pentagon rule (IPR) proved to be applicable to such large fullerene cages. For sufficiently large fullerenes like C₈₄, some isolated-pentagon isomers are also predicted to be very unstable with highly antiaromatic π bonds. © 1996 by John Wiley & Sons, Inc.

Introduction

Molecular clusters with up to several hundred carbon atoms are now being studied by vaporization of graphite in low-pressure helium.¹ Many different fullerenes are observable in the gas phase immediately following cluster for-

mation, but only a few are isolable. Thus, the range of kinetic stability or chemical reactivity of fullerenes is very wide. All isolated species are thermodynamically stable fullerene isomers. In addition, they obey the isolated pentagon rule (IPR), which states that stable fullerene molecules must have no abutting pentagons.²⁻⁵

It is generally accepted that fullerenes with no abutting pentagons are thermodynamically more stable than others because this arrangement minimizes the strain energy.²⁻⁷ Two fused pentagons

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form a local pentalene structure, which has a net destabilizing effect on the overall π electronic structure.^{3,4} It is interesting to note that these σ and π bonding effects work in the same direction, tending to keep the five-membered rings apart.^{4,5} We recently pointed out that CC bonds shared by two pentagons in IPR-violating or non-IPR fullerenes are very reactive in nature.⁸

The bond resonance energy (BRE) represents the contribution of a given π bond to the topological resonance energy (TRE).⁸ π Bonds with large negative BREs are antiaromatic in nature. Just as a highly antiaromatic molecule is very reactive in general,⁹⁻¹² a molecule with highly antiaromatic local structures must be very reactive and fragile. We previously applied the BRE concept to C_{70} and smaller fullerenes and found that CC bonds shared by two pentagons in non-IPR fullerenes are chemically reactive with large negative BREs.⁸ In this sense, non-IPR fullerenes are kinetically very unstable.

In this connection, chemical reactivity of buckminsterfullerene (C_{60})¹³⁻¹⁵ can be explained in the following way. This molecule has two nonidentical π bonds: 5/6 and 6/6 bonds. Here and hereafter, an m/n bond denotes the π bond shared by m - and n -membered rings. All 5/6 and 6/6 bonds in C_{60} are aromatic with positive BREs. The BREs of the 6/6 bonds ($0.193 |\beta|$) are larger than those of the 5/6 bonds ($0.082 |\beta|$).⁸ Therefore, when chemical reaction occurs, it progresses in such a manner that the product retains as many highly aromatic 6/6 bonds as possible. Insertion reactions tend to occur at a 5/6 bond,¹³⁻¹⁵ so that all 6/6 bonds are retained in the resulting π -electron system. Addition reactions occur predominantly at a 6/6 bond,¹³⁻¹⁵ so that only one 6/6 bond, together with four 5/6 bonds, is lost. If addition occurred at a 5/6 bond, two highly aromatic 6/6 bonds, together with three 5/6 bonds, would be lost.

For all non-IPR fullerenes investigated previously, 5/5 bonds are highly antiaromatic with very large negative BREs.⁸ Therefore, various chemical reactions are predicted to occur, in such a manner that they diminish the number of 5/5 bonds. Very small localization energies calculated for carbon atoms shared by two pentagons support this prediction.⁸ Electrophiles and nucleophiles must attack these carbon atoms preferentially and readily. Note that when an addition or insertion reaction occurs at a 5/5 bond, no highly aromatic 6/6 bonds are lost from the fullerene π -electron system.

For fullerenes larger than C_{70} , the number of IPR-observing or IPR isomers grows dramatically as the fullerene size increases. C_{84} is one of the most abundant fullerene molecules generated after C_{70} , and its structure has been the subject of extensive theoretical investigation.¹⁶⁻²⁶ Manolopoulos and Fowler showed that C_{84} has a total of 24 topologically distinct IPR isomers among thousands of possible configurations.²¹ Two of them have been isolated and the corresponding structural properties have been investigated by ^{13}C -nuclear magnetic resonance spectroscopy.²⁷⁻³¹ For predicting isolable isomers of such large fullerenes, one needs to know not only thermodynamic but also kinetic stabilities of many fullerene isomers. In this article, we evaluate the heats of formation and BREs of 73 typical C_{84} fullerene isomers to see if the IPR holds in general for large fullerenes.

Theory

Molecular mechanics calculations were carried out using the MM3(92) program³²⁻³⁴ to evaluate the heat of formation. The π -binding energy per carbon atom and the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy separation were calculated using simple Hückel molecular orbital (HMO) theory. A large HOMO-LUMO energy separation is conventionally associated with high kinetic stability because it is energetically unfavorable to add electrons to a high-lying HOMO, and extract electrons from a low-lying LUMO, and so to form the activated complex of any potential reaction.^{3,5,35}

The definition of the BRE⁸ is briefly repeated here. First, a secular equation is written for a given molecule with a total π -binding energy of E_0 . Then, one of the two off-diagonal elements corresponding to an arbitrarily chosen π bond in the molecule, say, the C_p-C_q bond, is multiplied by i , and the other by $-i$, where i is the square root of -1 .^{36,37} All other elements in the determinant are kept unchanged. The total π -binding energy obtained by solving this modified secular equation is denoted by E_{pq} , which is devoid of aromatic stabilization due to the circuits sharing the C_p-C_q bond. Therefore, the difference between E_0 and E_{pq} can be interpreted as a contribution of the C_p-C_q bond to aromaticity. It may be called the bond resonance energy (BRE) for the C_p-C_q bond. As pointed out previously,⁸ the BRE is a good index for predicting the kinetic stability or general chemical reactivity of individual π bonds.

Results and Discussion

Manolopoulos and Fowler numbered 24 topologically distinct IPR isomers in their study.²¹ We cite their isomer numbers in the first column of Table I. Before the experimental measurement of Kikuchi et al.²⁹ was published, theoretical calculations based on tight-binding molecular dynamics (TBMD),^{18,22} modified neglect of differential overlap (MNDO)¹⁹ and first-principle local-density functional²⁰ methods predicted that two of the IPR isomers, **22** and **23**, are most energetically favorable. A mixture of these two is consistent with ¹³C-NMR spectra.²⁹⁻³¹ In Table II, non-IPR isomers are numbered in order of decreasing π -binding energy per carbon atom.

MM3 heats of formation calculated for 24 IPR isomers of C₈₄³⁴ are listed in Table I. Of thousands

of non-IPR C₈₄ isomers, 49 can be derived easily by a single pyracylene transformation of the 24 IPR isomers.^{34,38} These constitute a group of rather spherical and energetically stable non-IPR isomers. Their heats of formation, calculated again using MM3, are listed in Table II. The present MM3 calculations support the view that two of the lowest-energy isomers, **22** and **23**, are very close in energy and similar in shape, indicating that they may form a mixture in synthesis. The distribution of heats of formation for 73 C₈₄ fullerene isomers is shown in Figure 1. Note that IPR isomers are not always lower in energy than non-IPR isomers.²³ The lowest-energy non-IPR isomer (**40**) is ca. 16 kcal/mol less stable than the lowest-energy IPR isomer (**22**).

HMO calculations are not useful for predicting the most thermodynamically stable C₈₄ isomers since σ strain has an important effect on the rela-

TABLE I.
IPR Isomers of C₈₄.

Species ^a	π -Binding energy per carbon atom ($ \beta $)	HOMO-LUMO energy separation ^b ($ \beta $)	Minimum BRE ($ \beta $)	Heat of formation ^c (kcal/mol)
1 (D ₂)	1.5590	0.6143 (1.28)	0.0819	742.59 (27)
20 (T _d)	1.5588	0.6962 (1.49)	0.0771	732.65 (14)
2 (C ₂)	1.5570	0.3523 (0.79)	-0.0390	737.63 (20)
18 (C _{2v})	1.5567	0.3285 (0.82)	-0.0543	726.02 (7)
14 (C _s)	1.5566	0.4054 (0.89)	0.0202	727.47 (8)
24 (D _{6h})	1.5565	0.5293 (1.14)	0.0351	721.99 (3)
4 (D _{2d})	1.5564	0.3519 (0.82)	0.0108	734.68 (17)
16 (C _s)	1.5559	0.3369 (0.81)	-0.0316	722.83 (4)
6 (C _{2v})	1.5555	0.1892 (0.53)	-0.0414	728.15 (9)
11 (C ₂)	1.5553	0.2540 (0.66)	-0.0501	723.89 (6)
19 (D _{3d})	1.5552	0.1861 (0.55)	-0.0702	723.53 (5)
22 (D ₂)	1.5549	0.3449 (0.823)	-0.0254	719.76 (1)
5 (D ₂)	1.5546	0.2403 (0.610)	-0.0574	732.23 (13)
23 (D _{2d})	1.5546	0.3449 (0.844)	-0.0564	719.99 (2)
17 (C _{2v})	1.5546	0.1745 (0.49)	-0.1084	731.64 (12)
8 (C ₂)	1.5541	0.1776 (0.34)	-0.0119	740.42 (23)
15 (C _s)	1.5540	0.2191 (0.55)	-0.0732	728.25 (10)
12 (C _i)	1.5540	0.2164 (0.53)	-0.0415	728.74 (11)
9 (C ₂)	1.5531	0.0556 (0.17)	-0.1561	741.68 (24)
3 (C _s)	1.5530	0.0191 (0.14)	-0.1615	746.42 (34)
7 (C _{2v})	1.5527	0.1892 (0.49)	-0.0748	735.61 (18)
13 (C ₂)	1.5526	0.0988 (0.31)	-0.1473	738.36 (21)
10 (C _s)	1.5523	0.0916 (0.22)	-0.0725	757.25 (52)
21 (D ₂)	1.5522	0.1381 (0.40)	-0.0401	733.32 (15)

^a The same reference numbers as given in ref. 21 are assigned to all IPR isomers of C₈₄.

^b Values in parentheses are the HOMO-LUMO energy separations in units of electronvolts calculated using the TBMD method.

^c Numbers in parentheses indicate the order of increasing heat of formation among the 73 C₈₄ isomers. For IPR isomers of C₈₄ with the number larger than 16, there are one or more thermodynamically more stable non-IPR isomers.

TABLE II.
Non-IPR Isomers of C₈₄.

Species ^a	π -Binding energy per carbon atom ($ \beta $)	HOMO-LUMO energy separation ($ \beta $)	Minimum BRE ($ \beta $)	Heat of formation ^b (kcal/mol)
25 (C ₁)	1.5570	0.3967	-0.0969	759.15 (53)
26 (C ₁)	1.5568	0.2885	-0.1866	776.90 (70)
27 (C ₁)	1.5567	0.3217	-0.1725	750.36 (36)
28 (C ₁)	1.5567	0.2649	-0.1838	755.48 (48)
29 (C _s)	1.5566	0.2940	-0.1798	744.95 (31)
30 (C ₁)	1.5565	0.2815	-0.1945	756.03 (50)
31 (C ₂)	1.5564	0.3195	-0.2015	765.38 (60)
32 (C ₂)	1.5560	0.3730	-0.1277	742.54 (26)
33 (C ₁)	1.5559	0.3217	-0.1475	755.49 (49)
34 (C ₁)	1.5554	0.2777	-0.1044	743.43 (29)
35 (C ₁)	1.5552	0.2868	-0.1656	748.66 (35)
36 (C ₁)	1.5549	0.2674	-0.1884	773.99 (67)
37 (C _{2v})	1.5548	0.2741	-0.1769	767.26 (62)
38 (C ₁)	1.5548	0.2437	-0.1747	751.29 (37)
39 (C ₁)	1.5548	0.2887	-0.1722	745.08 (32)
40 (C ₁)	1.5547	0.2719	-0.1559	737.52 (19)
41 (C ₁)	1.5546	0.2680	-0.0820	757.09 (51)
42 (C _s)	1.5545	0.1240	-0.1823	762.36 (56)
43 (C ₁)	1.5544	0.2425	-0.1953	739.84 (22)
44 (C ₁)	1.5544	0.1251	-0.2458	752.59 (42)
45 (C _{2v})	1.5543	0.1892	-0.1758	752.32 (40)
46 (C ₁)	1.5541	0.1244	-0.2564	764.68 (59)
47 (C ₁)	1.5541	0.1238	-0.2914	752.87 (44)
48 (C _{2v})	1.5541	0.2897	-0.1673	733.59 (16)
49 (C _s)	1.5540	0.1659	-0.2054	745.95 (33)
50 (C ₁)	1.5539	0.0958	-0.2626	754.35 (45)
51 (C ₁)	1.5537	0.1875	-0.1317	752.73 (43)
52 (C ₁)	1.5535	0.1902	-0.1887	743.10 (28)
53 (C ₁)	1.5532	0.0870	-0.1874	754.56 (46)
54 (C ₁)	1.5530	0.1007	-0.2104	751.59 (38)
55 (C ₁)	1.5529	0.2045	-0.2107	744.27 (30)
56 (C ₁)	1.5528	0.0659	-0.2391	751.61 (39)
57 (C _s)	1.5527	0.1031	-0.1867	742.43 (25)
58 (C ₁)	1.5525	0.1449	-0.2596	764.24 (58)
59 (C _s)	1.5525	0.0429	-0.2283	772.75 (66)
60 (C ₁)	1.5525	0.0507	-0.2928	771.99 (65)
61 (C ₁)	1.5523	0.0596	-0.1279	770.38 (64)
62 (C ₁)	1.5523	0.1058	-0.1769	754.61 (47)
63 (C ₁)	1.5521	0.1240	-0.2411	762.70 (57)
64 (C ₂)	1.5517	0.0399	-0.2612	780.47 (71)
65 (C ₁)	1.5516	0.1048	-0.2972	759.55 (54)
66 (C ₁)	1.5516	0.0795	-0.1734	768.13 (63)
67 (C _s)	1.5515	0.0199	-0.2272	785.14 (73)
68 (C ₁)	1.5514	0.1197	-0.2074	774.26 (68)
69 (C ₁)	1.5514	0.1378	-0.2493	752.41 (41)
70 (C _s)	1.5510	0.0693	-0.2299	774.76 (69)
71 (C _s)	1.5509	0.1607	-0.2119	784.05 (72)
72 (C ₁)	1.5506	0.1174	-0.1963	766.79 (61)
73 (C ₁)	1.5499	0.0277	-0.2429	761.83 (55)

^a Non-IPR isomers are arranged in order of decreasing π -binding energy per carbon atom. Reference numbers beginning at **25** are given in this order. A list of connectivities of carbon atoms in these C₈₄ isomers are available on request to J. A.

^b Numbers in parentheses indicate the order of increasing heat of formation among the 73 C₈₄ isomers. Non-IPR C₈₄ isomers with numbers less than 52 have one or more thermodynamically more stable IPR isomers.

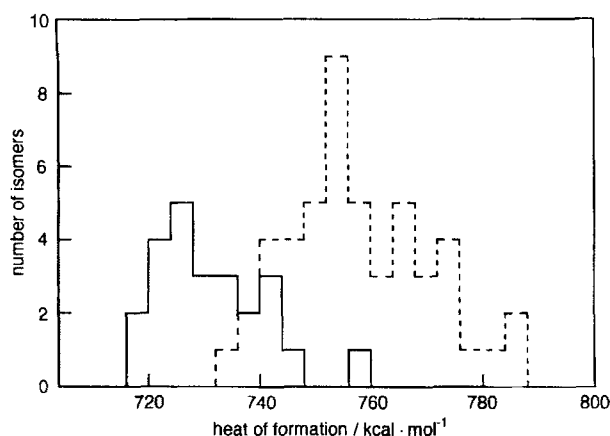


FIGURE 1. Distribution of the heat of formation among 73 C_{84} fullerene isomers. Solid and dashed lines indicate IPR and non-IPR isomers, respectively.

tive stabilities of the isomers.^{17,21} Low-energy fullerene isomers tend to distribute the pentagons as far apart as possible to minimize the local strains.^{19,20} Therefore, the isomers with the largest π -binding energies per carbon atom are not the most energetically stable ones. However, it is worth noting that the HOMO–LUMO energy separations of 24 IPR isomers calculated by HMO theory are highly correlative with those calculated by TBMD.¹⁸ As shown in Figure 2, the two sets of HOMO–LUMO energy separations exhibit a remarkably linear relationship. This indicates that high-lying molecular orbitals, which are primarily responsible for kinetic stability, consist mainly of carbon $2p_z$ orbitals. Thus, HMO is still very useful for describing π -electronic properties and kinetic stability of C_{84} fullerene isomers.

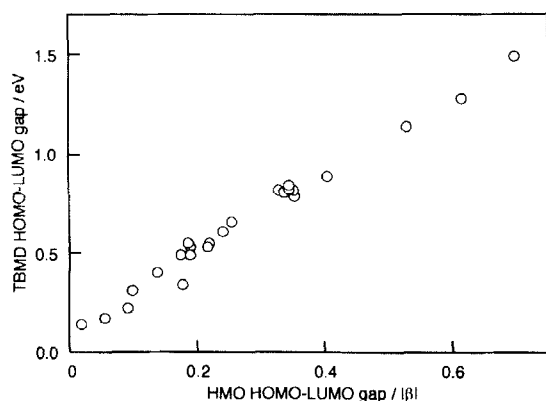


FIGURE 2. TBMD HOMO–LUMO energy separations versus HMO HOMO–LUMO separations. TBMD values were taken from ref. 18.

The preponderance of IPR isomers indicates a kinetic preference for isolation of these isomers.³⁹ Kinetic stability of a π -electron molecule is determined by the chemical reactivity of highly reactive sites in the molecule. The most reactive sites can possibly be related to the π bonds with the smallest or minimum BREs.⁸ If a molecule has π bonds with large negative BREs, there must be many reaction pathways to remove such antiaromatic π bonds from the molecule. The minimum BREs calculated for 1–73 are listed in Tables I and II. These minimum BREs lie in the range $+0.0819 \sim -0.2612 |\beta|$. π Bonds with large negative BREs represent highly reactive local structures in the molecule. The minimum BRE of $-0.10 |\beta|$ has been tentatively considered as a lower-limit value for kinetically stable or isolable fullerenes.⁸ All π bonds in two isolated isomers, 22 and 23, have BREs greater than $-0.10 |\beta|$. CC bonds with negative BREs in 22 and 23 are indicated in Figure 3.

Two isolated C_{84} fullerene isomers have lower heats of formation per carbon atom than C_{60} and C_{70} . However, C_{84} is formed in much lower yield by vaporization of graphite, which coincides with the fact that the minimum BREs of isolated C_{84} isomers are smaller than those of C_{60} and C_{70} . The minimum BREs of C_{60} and C_{70} are 0.082 and 0.052 $|\beta|$, respectively.⁸ C_{70} is almost always generated in substantially lower yield than C_{60} although the former species is thermodynamically more stable. Thus, it is clear that the yields of isolated fullerenes do not reflect a thermodynamic trend,³⁹ but may reflect in part kinetic stability.

CC bonds in fullerenes can be classified into three types: 6/6, 5/6, and 5/5 bonds. All 6/6 bonds in all C_{84} fullerene isomers are indeed aromatic with large positive BREs. The most kinetically unstable π bonds in IPR isomers of C_{84} are all 5/6 bonds. Most of the 5/6 bonds have small positive or negative BREs. Among the 24 IPR isomers, 1, 20, 14, 24, and 4 appear to be kinetically very stable since there are no antiaromatic π bonds. BREs of all CC bonds in these isomers are positive in sign. In addition, they have not only large π -binding energies per carbon atom but also large HOMO–LUMO energy separations. However, these IPR isomers have not been isolated because they are not thermodynamically very stable. Two isolated isomers, 22 and 23, do not belong to this group.

As in the case of C_{60} and C_{70} ,^{13,14} 23 reacts with some transition-metal compounds to give crystalline complexes. In an iridium complex of 23, the metal bridges a 6/6 bond connecting two pen-

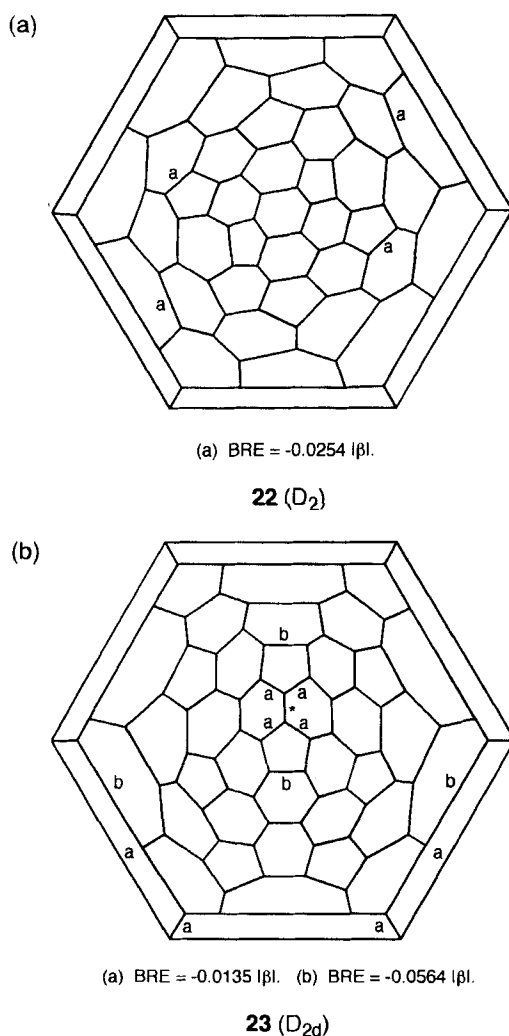


FIGURE 3. Antiaromatic π bonds in **22** (D_{2d}) and **23** (D_{2d}). The iridium binding site in a complex with **23** is denoted by *.

tagons,⁴⁰ in such a manner that four slightly antiaromatic 5/6 bonds, together with only one 6/6 bond, are removed simultaneously from the π -electron system. This is one of the best ways to minimize the loss of aromaticity. The iridium binding site in **23** is denoted by * in Figure 3.

Remember that the HOMO–LUMO energy separation and the minimum BRE can be regarded as measures of kinetic stability or chemical inertness. We found that for all IPR isomers of C_{84} , the minimum BRE is roughly correlative with the HOMO–LUMO energy gap. In general, an IPR isomer with a large minimum BRE has a large HOMO–LUMO energy separation. Such a situation is illustrated in Figure 4. Liu et al. presumed that fullerene isomers with a HOMO–LUMO gap

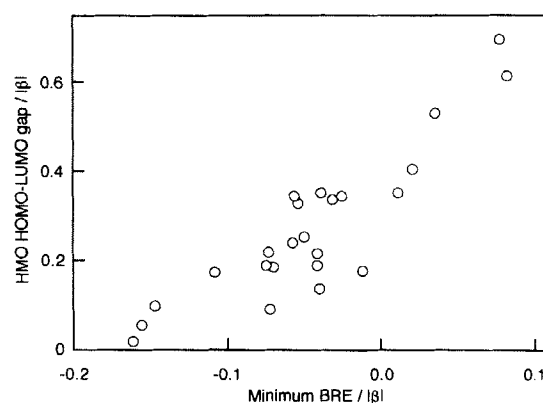


FIGURE 4. HMO HOMO–LUMO energy separations of C_{84} IPR isomers plotted against the minimum BREs.

greater than $0.344 |\beta|$ (the value for the known stable C_{76} molecule) will be stable against chemical reaction.⁵ Isolated C_{84} isomers, **22** and **23**, conform to this presumption although some other isomers also do.

It is interesting to note that IPR fullerene isomers are not always kinetically stable. If a given IPR isomer has not only a very small π -binding energy per carbon atom but also a small HOMO–LUMO energy separation, there is a possibility that some 5/6 bonds in the molecule are very reactive with a BRE less than $-0.10 |\beta|$. Among such unstable IPR isomers of C_{84} are **3**, **9**, and **13**. As these carbon cages have 5/6 bonds with very large negative BREs, they must have a marked olefinic character. These fullerenes presumably undergo various addition reactions, so that they eliminate such 5/6 bonds from the π -electron system. Among IPR isomers of C_{84} with sufficiently large π -binding energies per carbon atom, there are no such exceptions.

Next, let us examine the minimum BREs of non-IPR isomers. As in the case of smaller non-IPR fullerene isomers,⁸ all non-IPR C_{84} isomers studied are predicted to be very reactive with large negative minimum BREs. As shown in Table II, all non-IPR isomers have one or more 5/5 bonds with the BREs less than $-0.082 |\beta|$. This implies that 5/5 bonds, if any, are kinetically much less stable than olefinic CC bonds in acyclic polyenes. It follows that abutting pentagons are not favorable to the stabilization of the fullerene π -electron system.⁸ We can safely say that the IPR holds for such large fullerenes as C_{84} . At least, there are no particular reasons to believe that this rule does not apply to other large fullerenes.

One may note that two of the non-IPR isomers, **25** and **41**, have the minimum BREs slightly larger than $-0.10 |\beta|$. Nevertheless, we do not need to worry about them because these two isomers are thermodynamically very unstable. Presumably, they are not formed from the carbon vapor, so are not isolable anyway. The minimum BREs of all other non-IPR isomers are less than $-0.10 |\beta|$. Some non-IPR isomers, e.g., **40** and **43**, are thermodynamically more stable than some IPR isomers (e.g., **1** and **8**), but the former ones are kinetically much less stable. Figure 5 shows that for non-IPR isomers, the minimum BRE is not highly correlative with the HOMO–LUMO energy separation. Non-IPR isomers with a large negative minimum BRE have relatively small HOMO–LUMO energy gaps, but even those with large HOMO–LUMO energy separations are not kinetically stable. The HOMO–LUMO energy separations of **25** and **32** are greater than $0.344 |\beta|$, although they do not obey the IPR. Any IPR isomer has a much larger minimum BRE than non-IPR isomers with like HOMO–LUMO energy separations.

Finally, the degree of aromaticity is estimated for the C_{84} fullerene isomers. The percentage topological resonance energy (%TRE) is useful as a measure of aromaticity,^{41,42} which is defined as 100 times the TRE, divided by the π -binding energy of the polyene reference. It is easy to evaluate the TREs of relatively small molecules. However, the π -electron systems of C_{84} isomers are so large that the TRE cannot be obtained straightforwardly for any of them. Fortunately, there is an approximate but sufficiently reliable way to estimate the TRE. We note that the π -binding energy per carbon atom of the polyene reference for C_{60} ($1.52531 |\beta|$) is very close to that for C_{70} ($1.52540 |\beta|$),⁴³ so

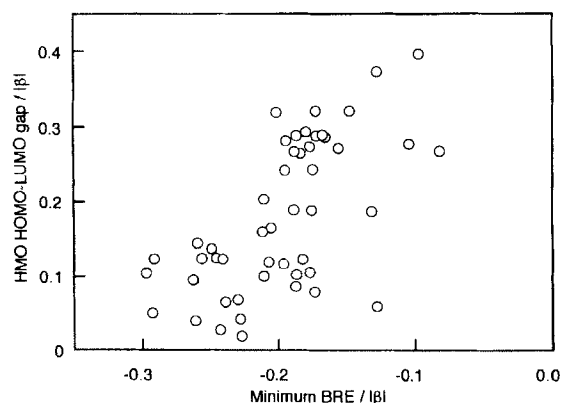


FIGURE 5. HMO HOMO–LUMO energy separations of C_{84} non-IPR isomers plotted against the minimum BREs.

must again be very close to those for C_{84} fullerene isomers. On this basis, the value for the C_{70} polyene reference can be used as an approximate π -binding energy per carbon atom of the polyene reference for all C_{84} fullerene isomers.

The %TREs of the isolated C_{84} fullerene isomers, **22** and **23**, were then calculated to be ca. 1.94 and 1.91, respectively. The %TREs of highly aromatic benzene and moderately aromatic C_{60} and C_{70} are 3.528, 1.795, and 1.906, respectively.^{41–44} Thus, these two C_{84} isomers turned out to be as moderately aromatic as C_{60} and C_{70} . Considering that even the isomer with the smallest π -binding energy in Table II, **73**, has a %TRE of 1.61, it is highly probable that all C_{84} fullerene isomers are moderately aromatic with moderately large positive %TREs. Accordingly, it is clear that antiaromaticity in the entire molecule is not responsible for the failure to isolate many large fullerene isomers.

Conclusions

We have shown that the IPR can safely be applied to large fullerenes, such as C_{84} . Large fullerenes have many IPR isomers, so the conformity to the IPR is not the only condition for determining isolable fullerene isomers. The present study gives credibility to our previous suggestion that thermodynamically very stable fullerene isomers are kinetically stable if there are no highly antiaromatic π bonds in the carbon cage.⁸ It does not seem that the HOMO–LUMO energy separation is a reliable measure of kinetic stability for non-IPR fullerene isomers. The BRE can be used for seeking the most reactive sites in a π -electron system and also for predicting the degree of kinetic stability.

All non-IPR fullerene isomers studied have very reactive 5/5 bonds with large negative BREs. Some IPR isomers of C_{84} must also be kinetically as unstable as non-IPR ones because some of the π bonds are highly antiaromatic. These exceptions indicate that the IPR is a necessary but not a sufficient condition for the kinetic stability of fullerenes. Fullerenes with highly antiaromatic π bonds must be incapable of survival during the synthetic process. Thus, the lowest-energy IPR isomers with a large π -binding energy per carbon atom must be dominant isolable products if they are isolable at all. As stated previously,⁸ even the lowest-energy fullerene isomers are not isolable at

least if they have antiaromatic CC bonds. C_{62} , C_{64} , C_{66} , and C_{68} are such examples.

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